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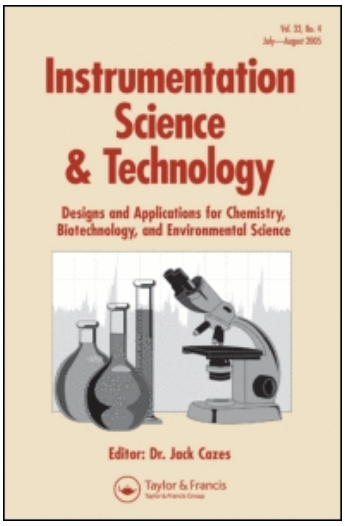

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Infrared Spectroscopy in Qualitative Analysis of Laser Printer and Photocopy Toner on Questioned Documents

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Abstract: A study was undertaken to examine the possibility of qualitative analysis of photocopy and laser printers toners by three different microscopic infrared spectrometry techniques: Diffuse Reflectance (DRIFTS), microscopic Attenuated Total Reflectance (μATR), and microscopic Reflection-Absorption (μRA), respectively, with a variety of reflecting media including mirrored slides, low emissive glass, or aluminum foil. Selection of the analysis technique can be made based on equipment availability, ease of sample preparation, speed of analysis, and importance of the original document to determine if a mildly destructive technique can be used.

Keywords: Attenuated total reflectance, Diffuse reflectance, Forensic science, Infrared microscopic spectrometry, Laser printer toner, Photocopies toner, Qualitative analysis, Reflection-absorption

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INTRODUCTION

Infrared spectrometry (IR) provides a useful way for the identification of different substances in forensic laboratories.[1–4] However, the traditional techniques employed to obtain the IR spectra, such as alkali halides disks, mulls, and thin films, are sometimes not adequate for quantitative analysis.

Forensic laboratories must often work with small samples in order to determine the type of material and its possible manufacturer for investigatory and evidence purposes. An example would be in the analysis of a photocopied document for the identification of the particular type of toner used in the generation of the document. The toners have different physical properties, which can help the analyst in tracking down of the origin of the document. Totty[5] reviewed analytical techniques that have been used to characterize toners.

Early work by Kemp and Totty[6] found that 79 toners from various models of photocopier machines could be separated into 10 groups, based on their IR spectra. Williams[7] identified numerous resins and the pigment, Prussian blue, based on characteristic IR absorptions. Zimmerman et al.[8] analyzed 35 toners by IR and determined 18 separate groups.

In routine examination of toners on questioned documents, nondestructive analytical methods, such as microscopic and optical techniques are first applied. However, they are often insufficient to identify the inks. In such cases, it is necessary to apply chemical methods that cause partial destruction of the examined material.

The greatest benefit of infrared microscopy is the ability to spatially discriminate regions or domains within a sample. By automating optical positioning, this newest generation of instruments has the potential to dramatically reduce data collection time and allows this powerful analysis to be performed routinely. Reflection analysis is an optically simpler technique that involves reflecting the infrared light off the sample. In this mode, the objective is to focus the light from the sample as well. This mode of analysis requires that the sample have certain properties that allow the infrared radiation to be reflected in one of several ways.

In order to realize an analytical characterization and discrimination of photocopy toners, using IR spectroscopy, three techniques were used, namely: Diffuse Reflectance (DRIFTS), microscopic Attenuated Total Reflectance (μATR) with a germanium Internal Reflection Element (IRE), and microscopic Reflection-Absorption (μR-A).[9]

There are several forms of reflectance that can occur, depending on the surface characteristics of the sample.

Specular reflectance occurs when the thick (a few mm) sample has a flat, smooth and glossy surface, causing the infrared energy to reflect off the front surface of the sample at the same angle as the incident light.

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Diffuse reflectance occurs when the sample has a rough surface, causing the infrared energy to reflect at angles other than the incident energy and from different locations within the sample. The accessories can be used for sample that are large enough and, thus, there is no need to focalize small areas. They give us information on a large area of the surface (about 2 mm). The analysis is direct on toner on paper.

Reflection absorption experiments involve mounting the sample on a reflective surface. The infrared energy passes back through the sample, reflects off of the reflective substrate, and is passed back through the sample effectively, approximating a double pass experiment.[10] Microscopic reflection-absorption by infrared spectroscopy (μR-A) was shown to be a viable technique for analyzing the polymer resins contained in dry black photocopy and printer toners. Samples were prepared using a heat transfer process to move the dry toner from documents to aluminum foil affixed to standard microscope slides. A variable temperature soldering iron, set at 250°C, was used to transfer the toner to the aluminum foil. The heat was applied to the back of the document containing the toner to be sampled, so most of the heat was dissipated before reaching the toner.

Attenuated total reflectance is applied to samples where the composition of the surface needs to be measured. This is especially useful when the sample is either too thick or cannot be destroyed, separated, or manipulated. It is applied to soft samples, which can achieve good contact with the crystal of the ATR objective. The only consideration to be borne in mind is the ability to obtain good optical contact between the surface of the sample and the germanium crystal.

Unprinted papers and printed samples were measured with the micro-ATR (μATR) technique because it is suitable for flexible and reflective surfaces like paper, and its small size enables good contact with the sample. In the μATR method, the penetration depth, D_p, of the IR beam into the coating depends on the wavelength, λ, the angle of the incident light beam, θ, the refractive indices of the ATR crystal, n_1, and the sample material, n_2. In the case of a germanium crystal, the penetration depth, D_p, of the IR beam varies between 0.18 and 1.0 μm. To improve the reproducibility of this method, several parallel measurements were made from each sample and the spectra were averaged. The downside of μATR in paper and print studies is the poor spectral resolution from strongly absorbing surfaces.

This paper deals with the chemical qualitative analysis of toners used in photocopying and laser printing processes by FTIR spectroscopy. The purpose of the work was: to determine if the spectrum of the toner extracted from a document is consistent with the corresponding spectrum of the raw toner powder, to determine whether IR spectra obtained for raw and processed toner can be differentiated from spectra obtained from other toners and, if the above are true, then it is possible to realize an

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analysis of toners on the basis of characteristic absorption bands in the IR spectra.[11,12]

EXPERIMENTAL

Apparatus

Micro-analysis was performed on a Spectrum GX II infrared spectrometer coupled with a Spectrum Spotlight Microscope (Perkin Elmer Instruments, USA). The spectrometer has a KBr beam splitter and an EverGlo IR source. The microscope has an MCT detector refrigerated with liquid nitrogen and an ATR objective of germanium. Infrared spectra were measured at a resolution of $16\,cm^{-1}$ in reflection mode and $8\,cm^{-1}$ in ATR mode. The range measured was between 4,000 and $650\,cm^{-1}$ and 256 scans were acquired as needed for each spectrum. The spectral data were processed with the Spectrum software (version 6.1, Perkin Elmer Instruments, USA).

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Procedures

Samples were placed on a motorized stage that has a positional accuracy of better than 1 micron. Z-axis positioning of the stage was obtained through an autofocus control accessory placed upon the mechanical coarse/fine control of the scope. The data collection, stage, and z-axis motion were controlled through the Spectrum software. Mapped spectra were obtained from 1.0 by 1.0 mm square areas through repetitive sample contact with the ATR and, respectively, Reflachromat objectives. The point spacing was 20 microns across the sample for a total of 100 points. Mapping was accomplished by using a computer controlled microscope stage. With this method, the measurement steps in the lateral direction can be determined at the desired resolution. Spectral maps of the sample surfaces can be acquired automatically.

Materials

The 54 samples of laser printer and photocopy toners used are from well-known manufacturers and can be divided in several groups, e.g.: polyester tip resin (8), styrene acrylic copolymer tip resin (38), methyl methacrylate tip resin (4), epoxy resin (2), and epoxy and acrylate resin (2). All the samples were studied using the three different infrared techniques (DRIFTS, μATR, and μR-A). The sample preparation is

simple, fast, and essentially nondestructive. In μR-A techniques, the document is still legible after transferring the toner sample and only minimal destruction is visible microscopically. Care should be taken when sampling two-sided documents to avoid direct contact between the soldering iron and toner on the back of the document being sampled.

RESULTS AND DISCUSSION

Figures 1–4 present the FTIR spectra of toners produced by Samsung, Xerox, and Canon.

The purpose of the work was to:

a) determine if the spectrum of the toner extracted from a document and measured by FTIR is consistent with the corresponding spectrum of the raw toner powder (Figs. 1a and 1c, there is no significant differentiation between spectra of raw and extracted toner). In Fig. 1b, we can observe the influence of cellulose with large stretching vibrations appearing from 3,600–3,000 cm^{-1} and the broad envelope from about 1,500–1,200 cm^{-1} includes the C−H bending. The C=O stretching vibrations are included in the envelope from 1,200–1,000 cm^{-1}. Also, we can differentiate toners from spectra obtained from toners used in other models of same brand and also from other machines of different brands.

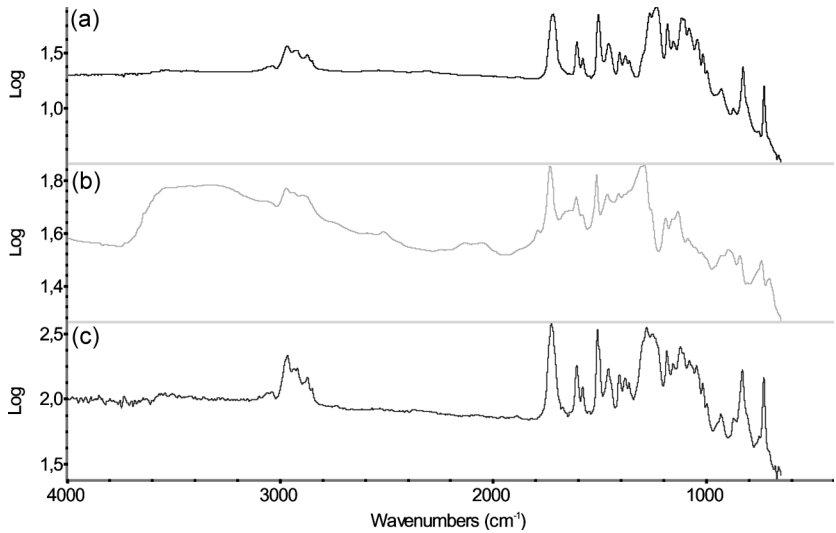

Figure 1. FTIR spectra of raw toner (a), toner on paper (b), and extracted toner (c) of Samsung ML 2570 toner.

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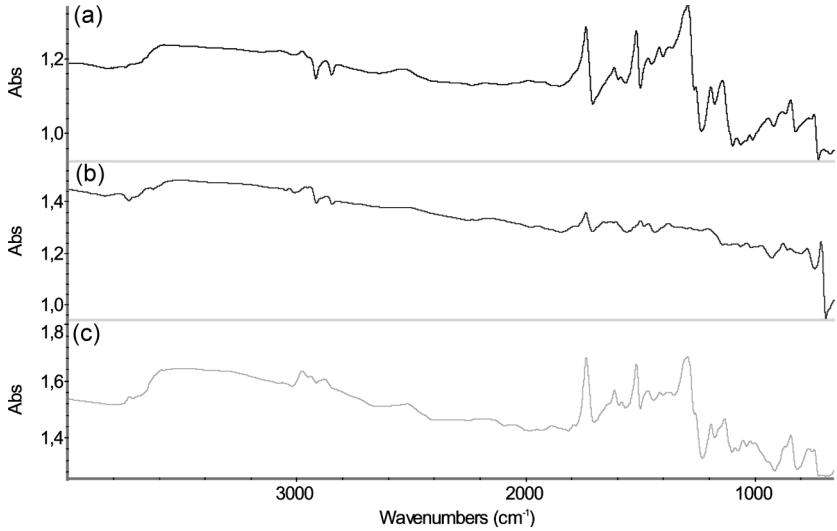

Figure 2. FTIR spectra of different printers using diffusion reflection technique: (a) Xerox Phaser 7700, (b) Canon LBP 5200, and (c) Samsung ML 2570.

b) if the above is true, then it is possible to devise a classification scheme for classifying toners used in photocopying and printing machines on the basis of characteristic absorption bands in the IR spectra.

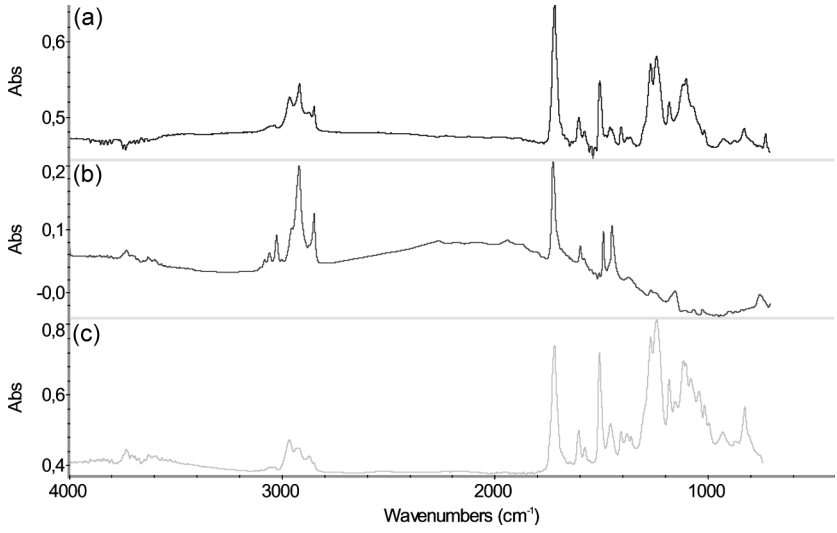

Figure 3. FTIR spectra of different printers using reflection-absorption technique: (a) Xerox Phaser 7700, (b) Canon LBP 5200, and (c) Samsung ML 2570.

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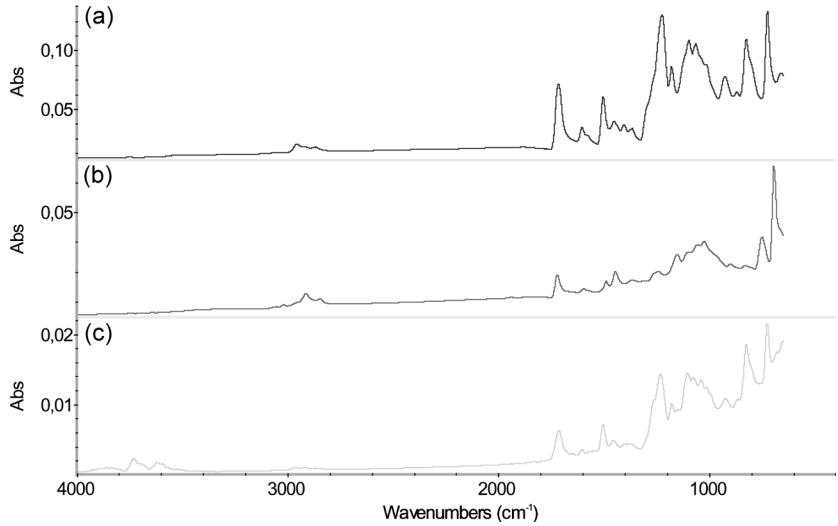

Figure 4. FTIR spectra of different printers using micro-ATR technique: (a) Xerox Phaser 7700, (b) Canon LBP 5200, and (c) Samsung ML 2570.

A searchable spectral library that contains 54 toner samples analyzed by each technique was created. A blind study was conducted to compare twenty documents, each paired to a test document, to determine if the pair could have been produced from the same machine.

Good spectral reproducibility, based on peak presence, has been demonstrated by analysis of sample smears obtained at different locations on the same document and from different documents generated by the same office machine using the same toner cartridge. Variations in peak height ratios have been observed, which suggests differences in concentration of some toner components. The correlation algorithm was used for searching the toner libraries that were created in this work.

Using the diffusion reflection technique, the analyst obtained 92% correct results in this study. Tests on thirty samples with the spectral library produced 90% first hits for the correct group. The three remaining samples were correctly determined by visual comparison of spectra for the top three hits. An actual case study was conducted where the investigation was narrowed from 200 possible machines to eight, based on a comparative study of the toners. We can properly differentiate the toners, with this technique, only in two regions: 3,000–1,500 cm^{-1} and 1,000–650 cm^{-1}, respectively (see Fig. 2).

Using the reflection-absorption technique, it was possible to differentiate 95% pairs of the examined samples using only FT-IR. Although a large number of groups were classified, only five general types of resins

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were identified. Based on our findings, styrene-co-acrylate resins make up approximately 75% percent of toners. There are minor differences noticed, sometimes, in the types of acrylates, comonomer concentrations, and additives that produce spectra differentiating the groups in the 1,700–1,000 cm^{-1}region. Figure 3 shows an identification of styrene-co-acrylate in the toner spectrum by the addition of an ester carbonyl near 1,720 cm^{-1} and the C–O–C stretch near 1,103 cm^{-1}.

Using the micro-ATR technique, for the initial testing of library searching, 40 samples were evaluated as unknowns by an analyst. Spectral library searching can be used to determine the possible group of manufacturer and model of copy machine. The toner spectra were collected, ATR correction applied, and a search was performed against the prepared spectral library. The recommended mode for searching the toner library consists of an initial search from 4,000 to 800 cm^{-1}. The strongly absorbing styrene bands that appear below 800 cm^{-1} on many of the toner spectra are often accompanied by severe anomalous dispersion inflections. The search results produced 32 first hits (80%) in the correct toner group. The remaining test spectra were compared with the spectra of the top 10 hits. The proper groups were identified from within the top three hits of the computer searches for the remaining samples (see Fig. 4).

Also, Fig. 5 indicates that two different cartridges of the same laser printer will produce identical spectra. The obtained spectra and all the

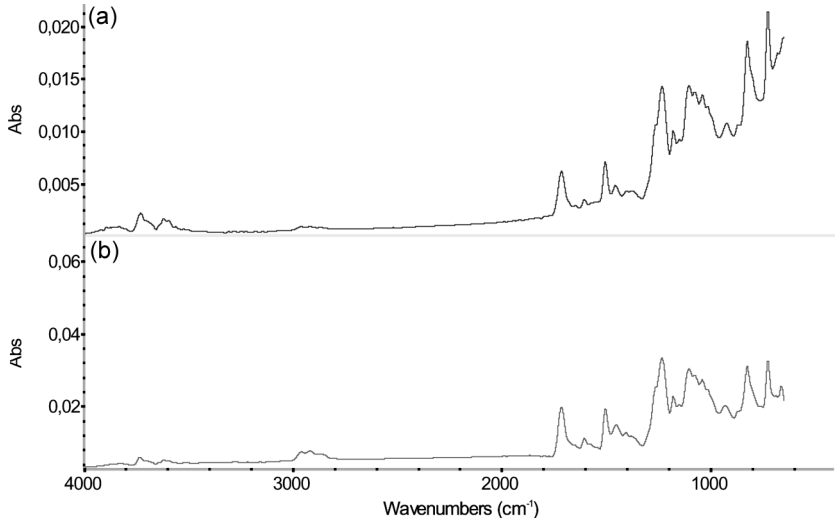

Figure 5. FTIR spectra of two different cartridges of the same printer Samsung ML 2570.

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available information could be used to create/build a database. Use of the spectral library assists with the identification of the toner group if the toner spectrum is included within the library. When comparing sample spectra to the spectral library, it is important to understand that the library is limited to toners produced by office equipment manufacturers specifically for use in their equipment.

Competitive manufacturers of toner for refilled cartridges are not included in the present spectral library but will be considered in a future study.

CONCLUSIONS

This study shows that toners can be differentiated by IR analysis, making it a potentially useful method for comparison of questioned documents. The results obtained confirm the multiplicity and compatibility of toners. The techniques are convenient, non-destructive, and often permit spectra of smears to be obtained in situ. The advantages of reflection include: little or no sample preparation, and fast sampling. To fully understand the significance of matched spectra of compared questioned and known documents, it will require us to conduct additional studies to determine variations between batches. This will need to repeat analysis of toners to determine the reproducibility of the toners and measurements.

Identification of a toner group may be useful as an investigative lead in some situations, although precautions are necessary. As mentioned above, analysis of replicate samples may be required to explain the occasional presence of extra absorptions consistent with non-homogeneous components.

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